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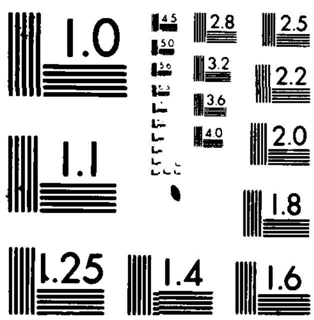

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Criterion for First-Order Phase Transitions*

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We show, via scaling arguments, that a first order transition occurs when the appropriate susceptibility (second derivative of the free energy) diverges proportional to the volume of the system. This result holds rigorously as an equality or an upper bound for a very large class of Hamiltonians. The divergence is maximal; therefore it provides a useful way of locating first order transitions. Our method gives accurate results for the two dimensional Ising model.

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We formulate, by means of a scaling argument, a general criterion for first order phase transitions in terms of the behavior of systems of finite size. This work is a natural extension of the ideas of Nienhuis and Nauenberg[1] on first order transitions in infinite systems and those of Nightingale[2] on calculating the critical temperature (and critical exponents) for higher order transitions from finite size results. In common with the latter and other recent works[3] we find that useful information about the thermodynamic limit can be obtained by comparing finite systems of different sizes. Further, we point out that our result is rigorously true for a very large class of ferromagnetic Ising models[4].

Our criterion provides a way of estimating the temperature at which a first order transition occurs from finite size results. It also implies that at a first order transition a second derivative of the free energy (such as the magnetic susceptibility) diverges proportional to the volume of the system. At a higher order transition, the corresponding argument indicates a less rapid divergence.

Our criterion is exact for the two dimensional Ising model[5]. We find, from finite size calculations, that the convergence is rapid and one can accurately locate the line of first-order transitions.

Our argument is quite general. However, for purposes of illustration, consider a magnetic system (e.g. the Ising model) of N spins in dimension d at temperatu[illegible] an external magnetic field h. Let $F_N(T, h)$ be the total free energy, $f \equiv F_N/N$ the free energy per spin, and $m(T,h)$ the magnetization per spin,

$$m = \frac{-\partial f}{\partial h}.$$

Now consider a similar magnetic system with N' spins at the same temperature T but some different external field h'. Then

$$F_N\,(T,h) = F_{N'}\,(T,h') + G(T,h) \qquad (1)$$

If $h = h'$, G is the free energy difference between the two systems. For $h \neq h'$, Eq (1) resembles the inhomogeneous scaling equation for the free energy in renormalization group theory[6]. Dividing by N we have

$$f(T,h) = \frac{1}{s^d}\, f(T,h') + g\,(T,h) \qquad (1a)$$

where $g = G/N$ and the scale factor $s \equiv (N/N')^{1/d}$. In Eq (1a) h' and g are not yet fully determined. Now take the thermodynamic limit $N,N' \to \infty$. We now make our main assumption, namely that near the transition (e.g. for small h) it is possible to pick h' so that h' and g are (sufficiently) regular functions of h (when $s<\infty$)[7,8].

Now for values of T for which a first-order transition exists, m will be a discontinuous function[9] of h at some point which we may take as $h = 0$. Differentiating Eq (1) with respect to h at $h = 0 \pm \epsilon$ we find

$$\Delta m = \frac{1}{s^d}\left(\frac{\partial h'}{\partial h}\right) \Delta m, \qquad (2)$$

where Δm is the discontinuity of the magnetization at temperature T. No term in $\partial g/\partial h$ appears in Eq. (2) since g is assumed regular at $h = 0$. Hence, at a first order transition in an infinite system,

$$\frac{\partial h'}{\partial h} = s^d \qquad (3)$$

This is essentially[10] the result of Nienhuis and Nauenberg[1,11]. When f is singular but m goes to zero as some power h^p ($p>0$, $p\neq$ integer), as it

does at a higher order phase transition, an extension of this argument shows that the power d in Eq(3) is replaced by $y = d/p+1 < d$. Thus the magnetic field is maximally renormalized at a first order phase transition[12].

It has been shown by Nightingale[2] and others[13] that very accurate results for the transition temperature and critical exponents at a higher order phase transition may be obtained from finite system results, by properly comparing two systems of nearby sizes[14]. The argument that follows extends Nightingale's method to first order transitions.

Consider Eq (1) for finite size systems. Differentiating with respect to the field, we have

$$m_N(h) = \frac{1}{S^d}\frac{\partial h'}{\partial h} m_{N'}(h') + \tilde{m}_N(h). \qquad (4)$$

The tilde in Eq (4) and below refers to derivatives of g. We have suppressed T and also the dependence of $\frac{\partial h'}{\partial h}$ on N and N'. In general, for finite N and N', all terms in Eq (4) are analytic. To obtain a useful result, we differentiate with respect to h once again. This gives

$$\chi_N(h) = \frac{1}{S^d}\left(\frac{\partial h'}{\partial h}\right)^2 \chi_{N'}(h') + \frac{1}{S^d}\frac{\partial^2 h'}{\partial h^2} m_{N'}(h') + \tilde{\chi}_N(h), \qquad (5)$$

where the magnetic susceptibility $\chi \equiv \partial m/\partial h = -\partial^2 f/\partial h^2$. Now $m_{N'}$ is (for most systems) bounded in the thermodynamic limit and by assumption $\tilde{\chi}$ and $\partial^2 h'/\partial h^2$ remain finite. At a first order phase transition, as N and N' $\to\infty$, χ will diverge and taking leading terms we have

$$\chi_N = \frac{1}{S^d}\left(\frac{\partial h'}{\partial h}\right)^2 \chi_{N'} = S^d \chi_{N'}$$

$$\chi_N = \frac{N}{N'} \chi_{N'} \qquad (6)$$

Note that if we are not at a first order transition, either we have a higher order transition for which $\partial h'/\partial h = S^y$, $y < d$, which results in a lower power[15] of N/N' in Eq (6), or else χ_N does not diverge at all. So we may write

$$\chi_N \leq \left(\frac{N}{N'}\right) \chi_N', \text{ for } N' < N, \tag{7}$$

where the equal sign holds for first order transitions only[16,17,18]. Thus Eq (7) provides a criterion for locating such transitions by comparing finite size results. It also provides a definition of a first order transition as a thermodynamic state for which the susceptibility diverges proportional to the volume of the system. Note that it implies that in such a state, a magnetic field of O(1/N) is sufficient to cause a finite magnetization in the thermodynamic limit[19].

To test the usefulness of our criterion (Eq. 7), we applied it to the two dimensional ferromagnetic Ising model on a lattice with square unit mesh with nearest neighbor spin coupling J = 1 and periodic boundary conditions[17]. This system has a line of first order phase transitions for (external field) h = 0 and $T < T_c = 2.269$ and a second order transition at $T = T_c$. Using the transfer matrix method, we determined χ_N for n x n lattices with n between 4 and 8 (note $N = n^2$). This was done by calculating m_N for sufficiently small h, so that the susceptibility could be obtained from $\chi_N = m_N/h$. For T values well above T_c, a plot of χ_N vs. N has a slope that decreases continually as N increases. For T well below T_c, χ_N becomes linear with increasing N, and the slope increases with decreasing T. The existence of a non-zero slope as $N \to \infty$ indicates (by Eq 7) that one is in a first-order transition region. As one moves out of such a region, the slope will drop more or less abruptly to zero. Finite size effects smooth out this drop. Hence the boundary of the region may be estimated by finding the inflection

point of $\frac{\partial\chi_N}{\partial N}$. Letting T_n^* be the temperature for which $\frac{\partial^2}{\partial T^2}(\frac{\partial\chi_N}{\partial N}) = 0$ we find, for the Ising model, $T_5^* = 2.40$, $T_6^* = 2.39$, $T_7^* = 2.37$, $T_8^* = 2.36$, compared to $T^* = 2.27$ for the infinite system[20].

A somewhat more accurate result may be obtained by calculating χ_n for an $n \times \infty$ strip of spins. Here, at a first order phase transition, χ_n may grow very rapidly with n since the system is unbounded in one direction. In such a region the system forms many domains of predominantly up or predominantly down spins. For a given value of n, at low enough temperatures, the domains will form a one dimensional array with average domain length (mean ordered length) $\ell_0 = \exp(\beta n\sigma)$, where σ is the free energy per spin of a domain wall[21]. Here one expects $\chi_n \cong n\,\ell_0$[22]. When one is not at a first order transition, χ_n will approach a constant value (or diverge less rapidly) as $n \to \infty$. The change-over to a divergent susceptibility whose rate of divergence increases rapidly with temperature should allow a more accurate location of the first order transition than for the $n \times n$ lattice, for which χ can diverge as n^2 at most. For the Ising model described on an $n \times \infty$ lattice, we find that at low temperatures $(\chi_n/n)^{1/n}$ apparently tends to a non-zero constant value with increasing n. Plotting $\Delta\chi_n \equiv \chi_n/n^2 - \chi_{n'}/(n')^2$, $n' = n-1$, one finds a change from negative $\Delta\chi$ values to positive $\Delta\chi$ values at the point where χ_n begins to diverge more rapidly than n^2. Defining T_n' as the temperature at which $\Delta\chi = 0$, we find $T_5' = 2.209$, $T_8' = 2.225$, $T_{10}' = 2.233$, compared to $T' = 2.269$ for the fully infinite lattice. In many systems it is not possible to calculate with one dimension infinite. However one can probably use a variant of this method with one dimension longer than the other (i.e. a rectangular or parallelpiped shaped lattice) to good advantage.

It is clear that our argument may be extended to systems other than Ising models[23,24]. In general, at a first-order phase transition there will

be an order parameter P[25] which is a discontinuous function of a conjugate thermodynamic field ξ, where

$$P = df/d\xi.$$

The discontinuity will occur in the infinite system. One expects that near the transition f has the shape of a roof top with $\xi = 0$ defining the ridge line. Then one finds, for the finite system, that Eq (6) will hold with χ replaced by $\partial^2 f/\partial^2\xi$. If ξ depends on the temperature, the entropy will be discontinuous - i.e. there will be a latent heat of transition[26]. In this case one expects that Eq (3) applies with h' and h replaced by T' and T, respectively, and Eq (6) applies for the specific heat C - i.e. C diverges proportional to the volume. Eq (3) then implies that the specific heat critical exponent $\alpha \to 1$ at a first order transition with latent heat. This conclusion has also been arrived at by Imry[27] by means of a plausibility argument for the finite size broadening of a first order phase transition.

We would like to thank G. Akinci for calculating the results for the n x n lattice reported above and for some very insightful remarks. It is also a pleasure to acknowledge useful discussions with R. B. Griffiths, M. E. Fisher, J. L. Lebowitz, E. Lieb, A. N. Berker and some helpful comments from one of the referees.

FOOTNOTES

1. B. Nienhuis and M. Nauenberg, Phys. Rev. Letters 35, 477 (1975).
2. M.P. Nightingale, Physica 83A, 561 (1976); Phys. Lett, 59A, 486 (1977); Proc. Kon. Ned. Akad. Wet. 82 series B, 235 (1979).
3. R.H. Swendsen, Phys. Rev. B20, 2080 (1979).
4. The result is also true as an upper bound (i.e. $\chi \leq Nm^2$, see below for notation) for lattice systems in which the order parameter is the expectation value of an operator that commutes with the rest of the Hamiltonian (R.B. Griffiths, Phys. Rev. 152, 240 (1966)).
5. T.D. Schultz, D.C. Mattis and E. Lieb, Rev. Mod. Phys. 38, 856 (1964) point out that the calculation of the magnetization of the two-dimensional Ising model by C.N. Yang, Phys. Rev. 85, 808 (1952) (and also that of E.W. Montroll, R.B. Potts, and J.C. Ward, J. Math. Phys. 4, 308 (1963)) is in fact a calculation of $\sqrt{\chi/N}$ for $N \to \infty$. Thus $\chi \propto N$ when $T < T_c$. This holds for periodic boundary conditions, for which the zerofield susceptibility per spin χ_N (see Eq (5) and below) may, since the magnetic field h is exactly zero, be written as a sum of N two-spin correlation functions $\langle S_i S_j \rangle$, since the magnetization m_N vanishes identically. This result may be extended to any Ising model in two dimensions with purely even ferromagnetic interactions including nearest neighbor exchange J and periodic boundary conditions by using the GKS inequalities (R.B. Griffiths, in Phase Transitions and Critical Phenomena, C. Domb and M.S. Green, eds., Academic Press (1972), Vol. 1, pp. 7-109) since each $\langle S_i S_j \rangle$ is bounded below by $\langle S_i S_j \rangle$ with J only. In three dimensions, one can embed a suitably deformed (to preserve the boundary conditions) plane including the points i and j for each term in the

sum. Then for $T < T_c^*$ one has $\chi \gtrsim N(m^*)^2$ where * refers to the 2d Ising model with interaction J only. Higher spin models may be treated using the transformation of Griffiths (op. cit. and J. Math. Phys. 10, 1559 (1969)). Note that the result $\chi \propto N$ does not follow from $\langle S_i S_j \rangle \to m_\infty^2$ as $N \to \infty$ since the range of distances $|i-j|$ over which this occurs may not grow sufficiently rapidly with N. However, the power N is clearly maximal whenever χ is a sum of (bounded) correlation functions (cf. footnote 4 and 12) since there are only N terms in the sum.

6. See, for instance, Th. Niemeijer and J.M.J. Van Leeuwen in Phase Transitions and Critical Phenomena Vol. 6, C. Domb and M.S. Green, eds., Academic, New York (1976).

7. For most applications of our criterion (see below) it is probably sufficient to let N - N' be fixed or otherwise such that as $N \to \infty$ our assumptions need only hold for $s \to 1$.

8. "Sufficiently regular" means that we require $\partial^2 h'/\partial h^2$ and $\partial^2 g/\partial h^2$ to be finite at the transition. Thus singularities appearing in higher derivatives of h' or g or essential singularities are compatible with our assumption.

9. This condition defines a first order phase transition for our purposes. Note that if, for small h, f has the simple form $f(T,h) = A(T) + (\Delta m(T)/2)\ |h| + B(T)h$, the conditions on h' and g are satisfied by $h' = s^d h$, $g = A(T)\ (1-s^{-d})$. This form for f is of course just one possibility and by no means unique.

10. Since our argument rests on a scaling assumption (Eq (1a) and ff) it is not necessary to invoke a complete microscopic renormalization

group mechanism as in ref. 1. Note also that our assumption that only one parameter (in this case h) is renormalized follows that of the phenomenological renormalization group treatment of Nightingale (ref. 2) for higher order transitions.

11. Note that Eqs. (1a) and (3) are consistent with assuming that the singular part of f is a homogeneous function of h with degree 1 at a first order phase transition. This assumption, in turn, is a special case of Widom's scaling equation of state given in J. Chem. Phys. 43, 3898 (1965).

12. In renormalization group theory, $y \leq d$ is a necessary condition for a physical spin coupling (one that does not grow with separation). In scaling theory, $y > d$ would imply that a first derivative of f is infinite at the transition, which is unphysical. (See also footnote 5).

13. W. Kinzel and M. Schick, Phys. Rev. B, to appear; L. Sneddon, J. Phys. C. 12, 3051 (1972); Z. Racz, Phys. Rev. B21, 4012 (1980).

14. As explained in ref. 2, one may regard the change in size of the system (from N to N' spins) as a renormalization group transformation with scale change s. Hence, one can in principle derive a scaling form for f at a first order transition by the standard argument (see ref. 4).

15. At a second order transition, S^d is replaced by $S^{2-\eta}$ in Eq (6). See M.E. Fisher in Critical Phenomena, M.S. Green, Ed., Academic, NY (1971).

16. If f has the simple form given in footnote 7, its singular part is $\propto |h|$. It is tempting to suppose that for finite N this is

simply replaced by $\sqrt{h^2 + h_{eff}(N)^2}$. Eq (6) then implies $h_{eff} \propto 1/N$, or more completely $h_{eff}=\Delta m/(2\chi_o N)$, where $\chi = \chi_o$ (T) N. For a transition with latent heat, this functional form leads to a finite size rounding ΔT_c of the transition temperature. Making the identification $T_{eff} \simeq \Delta T_c$, we find $\Delta T_c \propto 1/N$, in agreement with the result of Imry (ref. 27). His argument further implies that $T_{eff} \simeq kTc/(\Delta SN)$ where ΔS is the entropy discontinuity.

17. M.E. Fisher has remarked (private communication) that one must be extremely careful in choosing the proper boundary conditions in order that χ diverge $\propto$ N. We are indebted to one of the referees for pointing out that the intuitive requirement for this is that both phases be present with comparable probabilities - otherwise the variance of the order parameter will be greatly reduced. If for instance, one has an Ising model at h=0 with all boundary spins up, in general $m_N > 0$ and χ will not diverge. The work of J.L. Lebowitz, J. Stat. Phys. 16, 463 (1967) is interesting in this regard.
18. The result that χ diverges $\propto$ N as well as several other general features of first order phase transitions have recently been obtained by A.N. Berker and M.E. Fisher (unpublished).
19. This point has been demonstrated for the Kac model (a one dimensional Ising model with long range interactions) and the analagous point for the free Bose gas by Y. Imry, Ann. Phys. 51, 1 (1969).
20. Finding the inflection point of $\partial\chi_N/\partial_N$ with respect to $\beta = 1/k_B T$ instead of T increases the error in T_8^* by 50%.
21. L. Onsager, Phys. Rev. 65, 117 (1944).
22. It may seem somewhat inconsistent to use a semi-infinite system, for which our scaling argument does not apply, in order to get (improved) numerical

results. However, the same procedure is employed in the "phenomenological renormalization group" theory of Nightingale (Refs. 2 and 13). In this case one calculates the correlation length ξ as $1/\ln(\lambda_1/\lambda_0)$, where λ_0 is the largest and λ_1 the second largest eigenvalue of the transfer matrix. This formula gives the correlation length correctly for an $n \times \infty$ strip in a disordered region, and diverges $\propto n$ at a second order phase transition, in accord with scaling theory. However at a first order transition (e.g. for $h = 0$, $T < T_c$ in the Ising model), ξ calculated according to this formula diverges exponentially with n. This is because it is then a measure of the size of the ordered domains referred to above, closely related to the mean ordered length ℓ_0. Were one to calculate the correlation length on a finite lattice (e.g. an $n \times n$ square) it would in general diverge less rapidly (or not at all) in the first order region, and we expect this would reduce the accuracy with which the second order transition can be located, similarly to what we find herein for the first order case.

23. L.K. Runnels, J.R. Craig and H.R. Strieffer, J. Chem. Phys. 54, 2004 (1971) conclude that there is a first-order phase transition in a certain triangular lattice gas with hard cores on an $n \times \infty$ lattice. Their results indicate that at the transition the compressibility diverges faster than n^2 (as $n^{2.44}$) for a certain finite range of values of n, consistent with our results.

24. However, M.E. Fisher (private communication) suggests that there may be certain systems (e.g. with vector spins) for which $\Delta m \neq 0$ but χ does not diverge $\propto N$ (e.g. when the long-long range order vanishes). Thus although the derivation of Eq (6) is very general, its ultimate range of validity remains to be established.

25. Note that the definition of P may not be obvious in all cases e.g. if there is no obvious symmetry. This might pose a problem in the correct choice of boundary conditions (see Ref. 17).

26. A simple spin model illustrating this point is provided by R.B. Griffiths, Physica 33, 689 (1967).

27. Y. Imry, Phys. Rev. B21, 2042 (1980). It is easy to show that this work actually implies $c \cong (\Delta s)^2 N/k$, in agreement with Eq (6), where Δs is the entropy discontinuity.


8